U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
PB-294 734

A Problem with Flux Chamber Measurements of Biogenic Sulfur Emissions

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Prepared for

Environmental Sciences Research Lab, Research Triangle Park, NC

Apr 79

United States Environmental Protection Agency
Environmental Sciences Research Laboratory
Research Triangle Park NC 27711
EPA-600/3-79-033
April 1979
Research and Development
PB 294734

EPA

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films determines the transfer characteristics. It seems likely that in very still water, other factors such as the composition and thickness of the surface organic film microlayer may be more important (Liss, 1975). I know of no wind tunnel or field experiments relating gas emission rates to extremely low wind speeds. A second problem is that H_2S and perhaps other biogenic sulfides appear to be released in quantity from wet sediments exposed to the atmosphere. Film thicknesses under these circumstances are unlikely to vary with high speed in the manner implied by Liss's experimental data. A third problem is that there is always some gas-phase turbulence in the chamber, because the carrier gas is usually passed through the chamber in order to sample its composition. Some flux chambers employ a stirring device to ensure good mixing of the emitted gases in the carrier gas (Hill et al., 1978, Aneja et al., 1978) but others do not (Brannon, 1973, Adams et al., 1978, Hansen et al., 1978). Those who have used a stirrer have not reported the effects of stirring on emissions. Lacking any basis for an alternative procedure, I have therefore assumed for the purposes of this illustration that 'wind speed' inside the chamber is equal to zero, and that Equations 8 and 9 may be extrapolated to $\underline{u} = 0$.

Some of the problems introduced by these assumptions, and the difficulty of evaluating the effect of the use of chambers on H_2S emissions are due to the very large range of α values which are likely to be encountered in nature. τ and therefore α vary exponentially with pk_1, the first apparent dissociation constant for H_2S, since

$$pk_1 + \text{Log}\frac{[HS^-]}{[H_2S]} = pH \qquad \text{(Eq. 10)}$$

and pk_1 varies with T and chlorinity in seawater, and with T and ionic strength in freshwater. Goldhaber and Kaplan (1975) have shown that the value of pk_1 for seawater may be very accurately calculated from the following equation:

$$pk_{1(\text{seawater})} = 2.572 + 1359.96/T - 0.169\ Cl^{1/3} \qquad \text{(Eq. 11)}$$

where T is °K and Cl is chlorinity (°/$_{oo}$). Their work also suggests that this equation may be adapted to determine approximate values of pk_1 for freshwater as a function of ionic strength and T by assuming that freshwater

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TECHNICAL REPORT DATA
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1. REPORT NO. EPA-600/3-79-033	2.	3. RECIPIENT'S ACCESSION NO. PB294734
4. TITLE AND SUBTITLE A PROBLEM WITH FLUX CHAMBER MEASUREMENTS OF BIOGENIC SULFUR EMISSIONS		5. REPORT DATE April 1979 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Dian R. Hitchcock		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Hitchcock Associates Norton Lane Farmington, CT 06023		10. PROGRAM ELEMENT NO. 1AA603A AA-145 (FY-79) 11. CONTRACT/GRANT NO. DA-6-99-6358A
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Sciences Research Laboratory - RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711		13. TYPE OF REPORT AND PERIOD COVERED Final 7/76 to 10/76 14. SPONSORING AGENCY CODE EPA/600/09

15. SUPPLEMENTARY NOTES

16. ABSTRACT

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
*Air pollution Test chambers		13B
*Hydrogen sulfide		07B
*Organic sulfides		07C
*Biological productivity		08A
*Chemical analysis		07D
*Flux density		14B

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED 20. SECURITY CLASS *(This page)* UNCLASSIFIED	21. NO. OF PAGES 29 22. PRICE A03-A01

EPA Form 2220-1 (9-73)

EPA-600/3-79-033
April 1979

A PROBLEM WITH FLUX CHAMBER MEASUREMENTS OF BIOGENIC SULFUR EMISSIONS

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This report was submitted in fulfillment of Contract No. DA-6-99-6358A by Hitchcock Associates under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period July 2, 1976, to October 30, 1976.

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SECTION 1

INTRODUCTION

Biogenic sulfur gases may contribute significantly to the atmospheric load of sulfur species. This possibility has focused interest on the rate of emission of gases such as hydrogen sulfide (H_2S) and dimethyl sulfide (CH_3SCH_3) to the atmosphere from surface waters overlying sediments where they are naturally produced, or from exposed wet sediments. Several scientists have attempted to measure these emissions using emission flux chambers, a method by which gases released to the head space of a chamber placed over an emitting surface are collected by air or some other suitable carrier gas passing through; the average flux is then estimated from the measured concentrations of the gases of interest in the carrier gas. Such methods have been used by a number of researchers, including Brannon (1973), Aneja (1975), Hill et al. (1978), Adams et al. (1978), and Hansen et al. (1978).

The purpose of this report is to call attention to the possible influence of surface wind speed-induced liquid-phase turbulence on the evolution of H_2S and other gases from water surfaces. This study indicates that chambers which isolate emitting water surfaces from ambient wind movements may inhibit the evolution of H_2S, CH_3SCH_3, and other biogenic sulfur gases from surface water.

SECTION 2

METHODOLOGY

The general problem with the flux chamber technique is that isolating the emitting water surface will modify the exchange characteristics in ways presently impossible to fully evaluate. Liss (1973, 1975) explained some of these problems in his discussions of the applicability of Danckwaert's two-film model of gas exchange through the air-water interface to gas exchanges between natural waters and the atmosphere. (See also Deacon, 1977, for a more general treatment of these phenomena.)

TWO-FILM MODEL OF AIR-WATER EXCHANGE

The flux F of a gas through the air-water interface is the product of an exchange constant K for the gas and Δc, the difference between the concentration of the gas in the liquid near the interface and in the air above it:

$$F = K \Delta c \qquad \text{(Eq. 1)}$$

The model used by Liss provides that exchange takes place via molecular diffusion through two stagnant films at the air-water interface: a liquid film and a gas film. The overall exchange is described in terms of two transfer coefficients: the gas-phase transfer coefficient kg, and the liquid-phase transfer coefficient k_l, as well as the gas gradients within each film layer. However, as transfer between both films is limited by the slower of the two transfers through each, the exchange is spoken of as being 'controlled' by the slower of the two.

If exchange is controlled by liquid-phase resistance (assuming the gas obeys Henry's Law), then the overall exchange constant will be K_l, where

$$\frac{1}{K_l} = \frac{1}{K_l} + \frac{1}{Hk_g} \qquad \text{(Eq. 2)}$$

and H is the value of Henry's Law constant at the temperature (T) of interest. If exchange is controlled by gas-phase resistance, then the overall exchange constant will be K_g, where

$$\frac{1}{K_g} = \frac{1}{k_g} + \frac{H}{k_l} \qquad \text{(Eq. 3)}$$

To predict the value of K, the overall exchange constant for a given gas from these equations requires knowledge of their individual gas- and liquid-phase transfer coefficients k_g and k_l for the circumstances in question. Liss (1973) has shown that the transfer characteristics of gases in wind tunnel experiments may be predicted in terms of the gas-phase transfer coefficient $k_{g(H_2O)}$ for water vapor, and the liquid-phase transfer coefficient $k_{l(O_2)}$ for oxygen:

$$k_{g(X)} = rk_{g(H_2O)} \qquad \text{(Eq. 4)}$$

$$k_{l(X)} = \alpha k_{l(O_2)} \qquad \text{(Eq. 5)}$$

where X is the species of interest, r is the ratio of the square roots of the molecular weights of water and X, and α is an enhancement coefficient. If X is relatively unreactive and does not undergo rapid chemical reactions in water, then $\alpha = 1$. However, if X is subject to very rapid chemical reactions, then these will tend to increase its gradient in the liquid film, enhancing its transfer relative to O_2. The influence of enhancement will be a function of the speed of the reaction and the thickness of the liquid film. The most important chemical reactions leading to enhancement of transfer through the liquid film are dissociation and hydration. For gases such as sulfur dioxide (SO_2) and H_2S, for which these reactions are extremely rapid,

$$\alpha = \frac{\tau}{\tau - 1} \qquad \text{(Eq. 6)}$$

where τ is the ratio of total to ionic forms of the gas in water at the pH of interest. For H_2S in natural waters,

$$\tau = \frac{[H_2S] + [HS^-]}{[HS^-]} \qquad \text{(Eq. 7)}$$

because at pH ranges characteristic of natural waters, the sulfur is negligible.

For gases such as water vapor and SO_2, whose transfer is gas-phase controlled, the value of k_g varies with turbulence in the atmosphere near the surface of the water. Wind tunnel experiments have shown that $k_{g(H_2O)}$ varies directly with surface wind speed $\underline{u}$; the limited data available from field experiments confirm these observations (Liss, 1973, 1975, Hicks and Liss, 1976). However, in the field, the influence of fetch on the development of turbulence in the air near the air-water interface is important, and should be considered when predictions of $k_{g(X)}$ are made (Hicks and Liss, 1976).

The situation is considerably more complex for gases such as O_2, carbon dioxide (CO_2), H_2S, and most organic sulfides, whose transfer would seem to be liquid-phase controlled in most circumstances. Wind tunnel experiments indicate that $k_{l(O_2)}$ varies with the square of wind speed (Liss, 1973, 1975, Deacon, 1977), but the paucity of field data makes it difficult to evaluate the applicability of this model to the field. One problem is that liquid-phase controlled transfer is a function of turbulence in the liquid phase, and variations in surface wind speed are only one mechanism influencing liquid-phase turbulence. Turbulence induced by currents, surface ripples, or other motions in the water may also influence $k_{l(O_2)}$, as may differences between the temperature of the surface microlayer and the layers immediately beneath it (Liss, 1975, Deacon, 1977). It is also evident that water turbulence may have different effects on the absorption of a gas by the surface than on evolution from it. Thus, Liss (1973) found that breaking the surface of the water from below influenced release of O_2 from it more than absorption of O_2 by it. It is therefore evident that the

perturbations in gas-phase transfer caused by a chamber will vary with the manner in which it is used. Furthermcre, the limited information available about these phenomena only concerns transfer between water and air; no information is available about transfer between the surfaces of wet sediments and air.

SECTION 3

EXPERIMENTAL

CALCULATING THEORETICAL LIQUID-PHASE EXCHANGE CONSTANTS

The preceding discussion has shown that numerous uncertainties make it difficult to fully evaluate the possible chamber-induced perturbations in liquid-phase-controlled release of biogenic sulfides emitted from water or other wet surfaces to the air. However, some insight into the possible inhibition that may result from the use of flux chambers may be derived by comparing theoretical values of K_l calculated from Equations 2 through 7 above as a function of a hypothetical 'wind speed' inside and outside the chamber, using for this purpose the wind tunnel results of Liss (1973). There are, however, many problems associated with this approach.

Liss (1973) has determined the values of $k_{l(O_2)}$, $k_{l(CO_2)}$, and $k_{g(H_2O)}$ in wind tunnel experiments as a function of wind speed $\underline{u}$ for the range 1.6 to 8.1 m s^{-1} (where $\underline{u}$ is measured at 10 cm above the surface). In this range, $k_{l(O_2)}$ and $k_{g(H_2O)}$ are remarkably well described by the following linear equations:

$$k_{l(O_2)} = 0.52 + 0.165\ \underline{u}^2 \qquad \text{(Eq. 8)}$$

$$k_{g(H_2O)} = 18.6 + 1136\ \underline{u} \qquad \text{(Eq. 9)}$$

where k_l and k_g are in cm h^{-1}, and $\underline{u}$ in m s^{-1}. In applying these equations to the problem at hand, one must extrapolate them to a wind speed well below the minimum employed by Liss; it is highly unlikely that this extrapolation is valid. Not only is it well outside the range of the observations, but it also assumes that the notion of completely stagnant water is a physically realistic concept, and that in still water the thickness of the hypothetical stagnant

constitutes a very dilute solution of seawater. If so, then Equation 12 will be appropriate to many of the ionic strengths encountered in freshwater (about 0.05):

$$pk_{l(\text{freshwater})} = 2.35 + 1359.96/T \qquad \text{(Eq. 12)}$$

Because of exponential dependence of α on pH and T (see Figure 1), the value of $k_{l(H_2S)}$ may become very large at some pH and T values common in natural habitats. Consequently, at theoretical 'zero' wind speed when $k_{g(H_2O)} = 18.6$, the theoretical value of $K_{l(H_2S)}$ is determined by that of $k_{g(H_2S)}$. The extrapolations used in the above calculations imply that H_2S transfer may become gas-phase controlled inside the chamber, since

$$\frac{1}{K_{l(H_2S)}} = \frac{1}{\alpha k_{l(O_2)}} + \frac{1}{Hrk_{g(H_2O)}} \qquad \text{(Eq. 13)}$$

and the values of H employed for these calculations range from 0.2942 at 10°C to 0.5462 at 35°C. If this procedure is correct, it implies that in natural habitats, where gas-phase turbulence above the emitting surface may be low, H_2S transfer may be gas-phase limited. Therefore, the question of the influence of gas-phase turbulence on H_2S transfer cannot be ignored in considering the release of H_2S to the atmosphere, either in chambers or in the field.

Tables 1 and 2 list some theoretical values of $K_{l(H_2S)}$ calculated from the equations listed above. Values of $K_{l(CH_3SCH_3)}$ are also calculated as a function of wind speed, assuming a Henry's Law constant of 0.3, as given by Liss and Slater (1974). (Changes in the value of H with T will not influence the theoretical values of K_l for this gas, because its transfer is always liquid-phase controlled.)

Examination of these tables confirms that the emission rates of neither organic sulfides nor of H_2S observed inside flux chambers should be assumed to be representative of the emissions that might be occurring outside them. The liquid-phase controlled exchange constant varies exponentially with wind

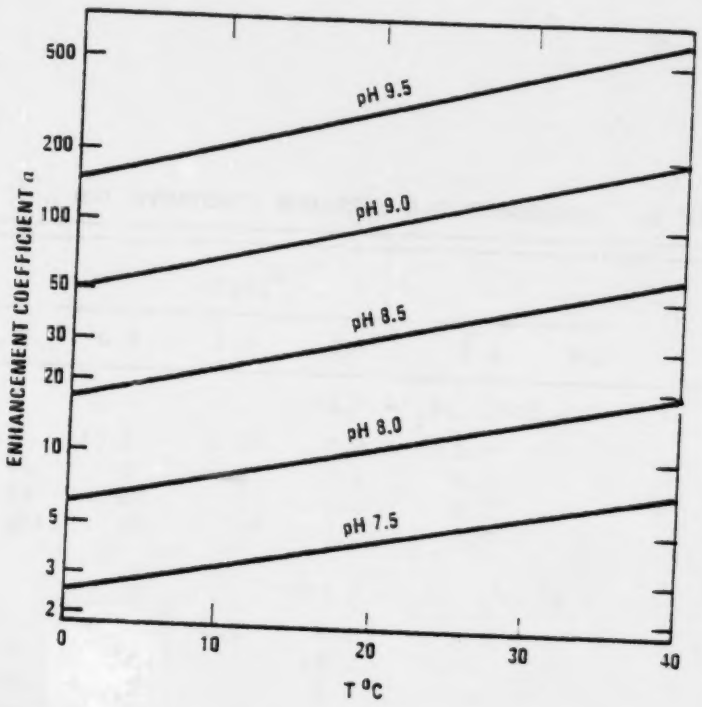

Figure 1. Enhancement coefficient α for H_2S transfer between seawater and air. (The dependence of α on pH and T is similar for freshwater transfer but calculated values are slightly lower than those plotted here.)

speed. In the case of unreactive organic sulfides, the apparent inhibition (calculated as the ratio of the exchange constant at a selected speed to that at 'zero' wind speed) ranges from about 3 at 2 m s^{-1} to about 16 at 6 m s^{-1}. In freshwater at pH values corresponding to relatively low concentrations of hydrogen sulfide ions (HS^-) relative to aqueous H_2S, the inhibition is similar to that for an unreactive organic sulfide. However, in freshwater at pH values above about 8, and in seawater at all pH values tabulated, emissions inside the chamber appear to be gas-phase controlled, and the inhibition effects are consequently larger and more variable, being critically dependent on α. Furthermore, where α is an important variable, the effects of pH are large. Thus, for freshwater (Table 1) at pH 8.0, the inhibition factors range from about 5 to 25 for $\underline{u}$ = 2 to 6 m s-1 at all temperatures shown. At pH 9.0, these inhibition factors range from 20 to about 100. In seawater (Table 2) the influence of pH is similar, but the inhibition factors tend to be larger. Thus, at pH 7.8, the inhibition factors range from about 5 to 26, but at pH 9.0 they range from about 35 to 150.

TABLE 1. FRESHWATER H_2S EXCHANGE CONSTANTS (cm h^{-1})

u	$K_{(CH_3SCH_3)}$	$K_{(H_2S)}$					
		pH 6.5	7.0	7.5	8.0	8.5	9.0
		T = 10°C pk_1 = 7.15					
0	0.4	0.6	0.7	1.2	2.0*	3.0*	3.6*
2	1.2	1.4	2.0	4	9	26	72
4	3.2	3.8	5.4	10	25	68	183
6	6.4	7.9	10.9	20	50	136	351
		T = 20°C pk_1 = 6.99					
0	0.4	0.6	0.9	1.6	2.8*	4.0*	4.8*
2	1.2	1.6	2.4	5	13	37	103
4	3.2	4.2	6.4	13	35	98	261
6	6.4	8.5	13.0	27	70	194	496
		T = 25°C pk_1 = 6.91					
0	0.4	0.6	1.0	1.8	3.2*	4.6*	5.4*
2	1.2	1.6	2.6	5.7	15	44	122
4	3.2	4.4	7.0	15.3	41	116	308
6	6.4	8.9	14.3	31.1	83	230	585
		T = 35°C pk_1 = 6.76					
0	0.4	0.7	1.2	2.3	4.2*	5.9*	6.8*
2	1.2	1.8	3.2	8	21	61	167
4	3.2	4.9	8.6	20	56	160	421
6	6.4	10.0	17.5	41	113	317	794

*Transfer is gas-phase controlled.

TABLE 2. SEAWATER H_2S EXCHANGE CONSTANTS (cm h^{-1})

u	$K_{(CH_3SCH_3)}$	$K_{(H_2S)}$				
pH		7.8	8.0	8.2	8.4	9.0
		T = 10°C pk_1 = 6.88				
0	0.4	2.0*	2.6	3.0*	3.3*	3.8*
2	1.2	11	16	25	37	119
4	3.2	29	43	65	97	294
6	6.4	58	86	129	192	541
		T = 20°C pk_1 = 6.80				
0	0.4	3.0*	3.5*	4.0*	4.4*	5.0*
2	1.2	15	23	35	54	169
4	3.2	40	61	93	139	415
6	6.4	81	123	184	274	758
		T = 25°C pk_1 = 6.64				
0	0.4	3.4*	4.0*	4.6*	5.0*	5.7*
2	1.2	18	27	42	64	199
4	3.2	48	72	110	165	487
6	6.4	96	145	218	324	887
		T = 35°C pk_1 = 6.49				
0	0.4	4.4	5.2	5.8	6.3	7.1
2	1.2	25	38	58	88	270
4	3.2	65	99	152	228	656
6	6.4	132	200	301	445	1185

*Transfer is gas-phase controlled.

These tables also show that the behavior of organic sulfides and H_2S inside a chamber cannot be readily interpreted as reflecting differences in their relative rates of release outside the chamber. At all T and pH values listed in both tables, the exchange constant for H_2S is larger than that for CH_3SCH_3, but the amount of the difference varies with pH and T. In freshwater, at pH values up to 7.5, the differences are small. At higher pH values, the differences become more pronounced, and they also increase with T. Thus, the H_2S transfer constant calculated for H_2S exceeds that calculated for CH_3SCH_3 by a factor of about 5 to 10 (depending on T) at pH 8.0, and by a factor of 6 to 17 at pH 9.0. The influence of pH and T are similar for seawater, but the differences are larger.

These calculations indicate a possible serious problem when interpreting flux chamber observations. As numerous uncertainties can be associated with the behavior of gases released from surface water and/or wet sediments, these results must not be viewed as constituting accurate descriptions of the processes occurring inside flux chambers, nor as providing useful predictions of the exchange process in the natural habitat.

These calculations do suggest, however, that in nature the release of H_2S from natural waters is an extremely complicated process. If H_2S release is as sensitive to pH, T, and liquid-phase turbulence as these calculations imply, then in some habitats actual releases must be very sensitive to short-term variations in turbulence induced by wave action, currents, and perhaps even disturbances of the surface due to biological activity. The rate of supply of H_2S to water near the surface is probably not as variable as its release from the surface to the air. It is possible that the concentration of H_2S in surface water could be highly variable, building up to relatively high levels if liquid-phase turbulence is minimal, and dropping rapidly as a response to emissions resulting from short-term disturbances of the surface. We may speculate that disturbances associated with putting a chamber in place could deplete H_2S concentrations significantly, and would be followed by low measured emissions until concentrations build up again. If so, then the total duration of the observations may be critical.

These calculations also show that the relative concentrations of organic sulfides and H_2S in surface water will rarely indicate the strength of their emissions. Especially when pH and T are high, a low concentration of H_2S may support a very large emission to the atmosphere, while much higher concentrations of CH_3SCH_3 may yield much lower emissions. These considerations throw doubt on the conclusions reported by Rasmussen (1974), who inferred that CH_3SCH_3 emissions from a small pond greatly exceeded H_2S emissions, because the CH_3SCH_3 concentrations were often one to two orders of magnitude higher than the H_2S concentrations. Examination of the original data (Bechard, 1974) shows that the values of the enhancement coefficients for H_2S were usually in the range 1000 to 3000, and that on the few occasions when the enhancement coefficients were less than about 10, the H_2S concentration exceeded the CH_3SCH_3 concentration. Viewed in this light, the observations reported by Rasmussen imply that the pond was a much larger source of atmospheric H_2S than of CH_3SCH_3.

TEMPERATURE AND PH VARIATIONS IN NATURE

A further cause for concern is associated with the influence of T and pH on H_2S evolution from surface waters, and the natural variation of these parameters in habitats of interest. Temperature and pH vary widely throughout the diurnal cycle in most habitats where H_2S is produced in abundance by the metabolism of the bacterial sulfate reducers, and from which it may escape to the atmosphere. In natural aquatic systems, pH varies with the concentration of CO_2, which in turn varies diurnally with the ratio of respiratory CO_2 production to photosynthetic CO_2 consumption. The more productive the habitat, the greater the diurnal range of pH values. In relatively shallow bays, creeks, marshes and similar aquatic systems, T varies diurnally with surface heating, and reaches its highest values in synchrony with pH. Skirrow (1965) measured summertime diurnal T and pH ranges from 28°C and 8.0 at night to 35°C and 8.9 the next day in highly productive water in Redfish Bay (Texas). The corresponding values of α are 42 and 258. In winter, the observed range was from 18°C and 8.0 at night to 23°C and 8.4 the next day (α equal to 29 and 54). In salt marsh pools and tidal creeks, the range of T and pH values may be greater, because plant productivity may make more demands on the supply of CO_2, and the very shallow waters get hotter than the surface waters of deeper bays. However,

in these habitats the temporal cycles are liable to be more complex, due to tidal effects. Very large pH and T variations are also likely to occur in some freshwater habitats. Bechard (1974) reports 67 measurements of pH, T, and sulfur gas concentrations in a freshwater pond; T values greater than or equal to 25°C were observed in 20% of these, and pH values greater than or equal to 9.5 in 30%.

Temperature is usually reported by many who employ the flux chamber technique, but not the pH or sediment or water H_2S concentrations. (Brannon, 1973, and Hansen et al., 1978, are exceptions.) As a result, one cannot determine whether the flux measurements some researchers report reflect variations in the relative productivity of H_2S (and/or other biogenic sulfides), variations in pH, or both. Consequently, even if the chamber method were demonstrated to have little significant effect on the transfer coefficients for these or other gases in some habitats of interest, many results reported in the literature could not be extrapolated to other times when the emitting surface may have other T and pH values.

These studies may be contrasted with those of Hansen et al. (1978), who used a flux chamber to study the emission of H_2S from two tide pools. They determined H_2S emissions at hourly intervals for durations of at least 24 hours, and monitored light intensity, surface water pH, T, H_2S and O_2 concentrations, and redox potential gradients in both water and underlying sediment as a function of depth. In addition, they characterized the sediments in biologically meaningful ways (sediment grain size, organic matter content and distribution, H_2S and sulfate (SO_4^{2-}) concentrations, and biological H_2S production as a function of sediment depth). These authors reported the observed H_2S emissions in relevant units ($\mu M\ m^{-2}h^{-1}$, rather than $g\ m^{-2}y^{-1}$) and related the variations in emissions to variations in other relevant parameters. The observed emissions were accurately characterized as "minimum emissions from stagnant water". In consequence, this study provides much valuable information, even though the H_2S emissions may not be representative of emissions outside the chamber.

POSSIBLE EFFECT OF H_2S EVOLUTION INHIBITION ON ITS AQUATIC FATE

Unlike CH_3SCH_3 and most other organic sulfide gases which are stable in water, H_2S may be oxidized by aqueous O_2. The reactions involved have not been studied in detail, but the limited evidence available indicates that they are extremely complex. Reported H_2S half-lives in natural waters range from about 20 minutes (Östlund and Alexander, 1963) to over 100 hours (Skopintsev et al., 1964), but 2 to about 20 hours appear to be the most common values (Cline, 1968, Cline and Richards, 1969, Bella, 1975, Wheatland, 1954, Almgren and Hagström, 1974). Hydrogen sulfide aqueous oxidation may be catalyzed by a number of transition series metals, and inhibited or catalyzed by organic substances (Chen, 1970, Cline, 1968, Cline and Richards, 1969). There is good evidence that the uncatalyzed reaction occurring in distilled water is less than first order in sulfide and greater than first order in O_2 (Chen, 1970), and suggestive evidence that this may be the case in some natural seawater systems (Broenkow, 1969). The oxidation products include sulfite, sulfate, sulfur, thiosulfate, and a number of polythionates; the relative abundance of these depends in part on the ratio of H_2S to O_2 (Chen, 1970, Cline, 1968, Cline and Richards, 1969).

On the basis of these reports one may speculate that, if inhibition of H_2S transfer to the atmosphere occurs in flux chambers, then a greater proportion of the H_2S present in the water may be lost through aqueous oxidation than would otherwise be the case. It is possible that H_2S oxidation products could then react with organic substances present in sediments and surface waters where H_2S is produced to form organic sulfide gases (Hitchcock, 1976). The latter speculation is further strengthened by the results reported by Hill et al. (1978), and Adams et al. (1978), who found that CH_3SCH_3 was released in relatively large quantities (on the order of 0.1 mg $m^{-2}h^{-1}$) in the daytime from Spartina alterniflora sediments. Rasmussen (1974) reports that he found high concentrations of CH_3SCH_3 in water or in the head space of cultures of decaying freshwater algae species when the use of a cotton stopper permitted some entry of O_2, but only H_2S when the culture was isolated from the atmosphere and the oxygen concentrations in the head space dropped (see also Lovelock et al., 1972).

The authors of these reports attribute the CH_3SCH_3 to the bacterial decomposition of organic sulfur present in decaying plant matter. However, this explanation seems unlikely on quantitative grounds. Organic sulfur in plants is present only in trace quantities (chiefly in amino acids); during decomposition very little of it is released as an organic sulfide gas. Lovelock et al. (1972) measured CH_3SCH_3 release rates in a number of substances. These rates, corrected for organic sulfur concentrations in the substrate, imply release rates of about 10^{-11}g g^{-1} of organic sulfur h^{-1} or less. This, in turn, suggests that the average CH_3SCH_3 release from organic sulfur decomposition in Spartina sediments may be about 0.001 µg $m^{-2}h^{-1}$, assuming organic sulfur concentrations in soils are as high as 100 g m^{-2} (an estimate that assumes a very large organic sulfur standing crop in bacterial tissue). The production rates are far too low to account for the observed organic sulfide releases; therefore, their source must be sought for elsewhere. The only other source is the H_2S which is produced in these soils in enormous quantities by bacterial sulfate reducers.

The dependence of CH_3SCH_3 concentration or release on O_2 availability, observed by Rasmussen (1974) and Lovelock et al. (1972), point to a possible source: a reaction between an H_2S oxidation product and other constituents normally present in muck soils and other habitats where bacteriogenic H_2S is produced in quantity. Thus, sulfite, polythionates, or elemental sulfur may react with organic acids or hydrocarbons to yield CH_3SCH_3 and possibly other organic sulfides in the quantities necessary to support the observed emissions.

This line of reasoning suggests that inhibition of H_2S evolution from surface waters or even from surface sediments could promote its aqueous oxidation. This process could conceivably result in the partial transformation of H_2S into organic sulfides.

SECTION 4

CONCLUSIONS

The foregoing discussion has demonstrated that there are great uncertainties regarding the use of flux chamber measurements to estimate the flux of biogenic gases from aquatic habitats to the atmosphere. These include the nature and magnitude of the effect of chambers on the transfer constants describing release to the atmosphere of H_2S and inert gases. The extreme variability of T and pH in natural habitats of interest also makes extrapolations from chamber observations to other times extremely questionable.

Until research on mechanisms influencing liquid-phase controlled transfer of gases from water surfaces and wet sediments demonstrates otherwise, flux chamber measurements cannot be regarded as providing reliable estimates of the rate of evolution of H_2S or other biogenic sulfides to the atmosphere. For the present, chambers should be regarded as useful ancillary tools to be used in the context of well-controlled studies that characterize and carefully monitor the physical and biological characteristics of the systems being examined. Furthermore, the concentrations of gases in the sediment or water under study should be monitored together with T, pH, and the very numerous other chemical properties known to influence the biological production and chemical fate of bacteriogenic sulfides.

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